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(71)Applicant : NIPPON SHOKUBAI CO LTD

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(72)Inventor : AOYAMA TAKAHIRO

NISHIDA TOSHIBUMI

NODA NOBUHISA

MASUDA SEIJI

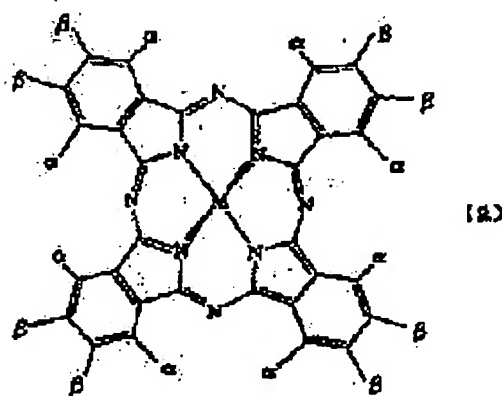
KITAO MASUAKI

(54) NEAR INFRARED ABSORBING FILM AND NEAR INFRARED ABSORBING RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a near infrared absorbing film having suppressed deterioration of a near infrared absorbing dye and excellent weather resistance and a near infrared absorbing resin composition.

SOLUTION: This near infrared absorbing film comprises a near infrared dye having 780-1,200 nm maximum absorption wavelength and $\geq 50\%$ residual ratio of near infrared absorptivity after light irradiation for 48 h in accelerated weathering tests with an ultraviolet auto fade meter. The film usually comprises a near infrared absorbing resin composition containing a polymer prepared by polymerizing a monomer component containing ≥ 30 mass% of a monomer represented by general formula (1) $\text{CH}_2=\text{C}(\text{R}_4)-\text{CO}-\text{OZ}$ (1) (wherein, R_4 is H or methyl group; and Z is a 4-25C hydrocarbon group). The dye is a compound



represented by general formula (2) (α is SR1, OR2, NHR3 or a halogen; NHR3 is essential; R1 to R3 are each phenyl group, an alkyl group or an aralkyl group; β is SR1, OR2 or a halogen; SR1 or OR2 is essential; and M is a metal or the like).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a near infrared ray absorptivity paint film and a near infrared ray absorptivity resin constituent.

[0002]

[Description of the Prior Art] A near infrared ray absorptivity resin constituent can form the film and coating film which have the property which absorbs the near infrared ray which is a heat ray, and attracts attention from a viewpoint of energy saving in recent years as a heat ray absorption film with which such a film and the coating film cover a heat ray, and prevent a temperature rise. For example, stick on a windowpane etc. the heat ray absorption film formed from a near infrared ray absorptivity resin constituent, or it puts between the glass of two sheets, and is used for a building, the residence, the car, the arcade, the greenhouse, etc. by applying to a windowpane etc. by making a near infrared ray absorptivity resin constituent into a coating agent, and making a heat ray absorption film form etc.

[0003] Such a near infrared ray absorptivity resin constituent is prepared by making a heat ray absorbent and binder resin contain in usual, and an inorganic system particle and organic system coloring matter are used as a heat ray absorbent. However, by the inorganic system particle, there was a problem that near infrared ray absorptivity ability with a wavelength of 1000nm or less was low, and could not fully prevent a temperature rise from a viewpoint of energy saving. Moreover, with organic system coloring matter, since near infrared ray absorptivity ability was gradually lost by sunlight etc. in a heat ray absorption film, as weatherability of a heat ray absorption film, it was not enough, and there was room of the research for making near infrared ray absorptivity ability maintain.

[0004] The layered product which equipped JP,2000-177064,A with the heat ray shielding layer containing a transparence base material, an ultraviolet-rays shielding layer, and heat ray shielding material is indicated. In this layered product, it has controlled that the heat ray shielding material contained in a heat ray shielding layer deteriorates by forming an ultraviolet-rays shielding layer in an optical incidence side rather than a heat ray shielding layer. However, there was room of the research for controlling degradation of heat ray shielding material and making the electric shielding engine performance of a heat ray maintain that it is simpler and certainly by devising the heat ray shielding layer itself.

[0005]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above, and aims to let it offer the near infrared ray absorptivity paint film and near infrared ray absorptivity resin constituent which can demonstrate the weatherability which was controlled and was excellent that near infrared ray absorptivity coloring matter deteriorates.

[0006]

[Means for Solving the Problem] This invention is a near infrared ray absorptivity paint film containing the near infrared ray absorptivity coloring matter which has absorption maximum wavelength in 780nm - 1200nm, and is a near infrared ray absorptivity paint film whose near infrared ray absorbing-power

survival rate 48 hours [in the accelerated weathering test in ultraviolet-rays auto fade meter] after an optical exposure is 50% or more.

[0007] The time that this invention persons examine many things about the near infrared ray absorptivity resin constituent which forms a near infrared ray absorptivity paint film and a heat ray absorption film, If the content of the water in a near infrared ray absorptivity paint film is decreased paying attention to the water contained in such a near infrared ray absorptivity paint film being one of the causes which degrades near infrared ray absorptivity coloring matter It found out that degradation of near infrared ray absorptivity coloring matter could be controlled, and hit on an idea for the above-mentioned technical problem to be splendidly solvable. Consequently, the layered product which has near infrared ray absorptivity ability can be used now for various applications, and this invention is reached. Below, this invention is explained in full detail.

[0008] The near infrared ray absorptivity paint film of this invention is a paint film containing the near infrared ray absorptivity coloring matter which has absorption maximum wavelength in 780nm - 1200nm. Such a near infrared ray absorptivity paint film will be formed with the near infrared ray absorptivity resin constituent which comes to contain the above-mentioned near infrared ray absorptivity coloring matter and binder resin. The above-mentioned near infrared ray absorptivity coloring matter is coloring matter which has absorption maximum wavelength, may be independently used for 780-1200nm, and may use two or more sorts together. When two or more sorts from which the absorption property of a near infrared ray differs are used together, the absorption effect of a near infrared ray may improve. In addition, near infrared ray absorptivity is used in semantics equivalent to heat ray absorptivity. Moreover, the above-mentioned binder resin makes a polymer indispensable, may be constituted by containing an organic solvent and a partial saturation monomer as occasion demands, may be used independently, and may use two or more sorts together.

[0009] It is desirable to use the coloring matter which has the solubility to an organic solvent, i.e., the near infrared ray absorptivity coloring matter of organic solvent fusibility, as near infrared ray absorptivity coloring matter in this invention. Since coloring matter can dissolve easily that it is meltable in an organic solvent into a binder resin solution, creation of a coating agent becomes easy. On the other hand, since mixing to a binder resin solution will become difficult if coloring matter is lacking in solubility, it becomes difficult [creation of a coating agent]. It is suitable to use the near infrared ray absorptivity coloring matter whose solubility which made the organic solvent 100 mass % is more than 0.01 mass % as solubility to an organic solvent. It is not limited especially as an organic solvent in organic solvent fusibility, for example, one sort [, such as ketone solvent; dimethylformamide,], such as ester solvent; acetones, such as alcoholic solvent; butyl acetate, such as aromatic series system solvent; iso-propyl alcohol, such as toluene and a xylene, n-butyl alcohol, propylene glycol methyl ether, and dipropylene glycol methyl ether, ethyl acetate, and a cellosolve acetate, a methyl ethyl ketone, and methyl isobutyl ketone, or two sorts or more are mentioned.

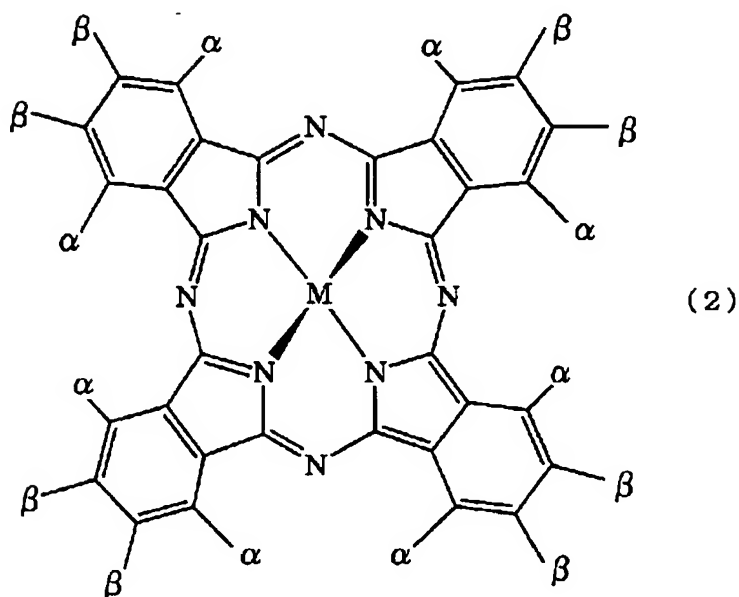
[0010] It is desirable to use phthalocyanine system coloring matter as a class of the above-mentioned near infrared ray absorptivity coloring matter, for example, since it excels in near infrared ray absorptivity ability and organic solvent fusibility also in these although phthalocyanine system coloring matter, naphthalocyanine system coloring matter, anthraquinone system coloring matter, naphthoquinone system coloring matter, etc. are mentioned.

[0011] The phthalocyanine system in this specification refers to a phthalocyanine, a phthalocyanine complex or a phthalocyanine, and a phthalocyanine complex, and it has one or more sorts of one or more substituents of OR, SR, NHR, or NRR' on the benzene ring of a phthalocyanine frame. R and R' expresses the aralkyl radical of the same, or the phenyl group which may differ and may have a substituent, the alkyl group of carbon numbers 1-20 or carbon numbers 7-20 here. In addition, it is desirable that one in a substituent is the phthalocyanine permuted by NHR.

[0012] It sets to this invention and the above-mentioned near infrared ray absorptivity coloring matter is the following general formula (2).;

[0013]

[Formula 4]



[0014] the inside of a formula and alpha are the same -- or it differs, SR1, OR2, NHR3, or a halogen atom is expressed, and NHR3 is made indispensable. R1 and R2 And R3 The aralkyl radical of the same, or the phenyl group which may differ and may have a substituent, the alkyl group of carbon numbers 1-20 or carbon numbers 7-20 is expressed. beta is the same -- or -- differing -- SR1 and OR2 or a halogen atom -- expressing -- SR1 Or OR2 Suppose that it is indispensable. However, at least one of alpha and beta is a halogen atom or OR2. Suppose that it is indispensable. M expresses a non-metal, a metal, a metallic oxide, or a metal halogenide. It is desirable that it is the compound expressed. Thereby, the operation effectiveness of this invention can more fully be demonstrated.

[0015] In the above-mentioned general formula (2) as an alkyl group of carbon numbers 1-20 For example, a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, An isobutyl radical, sec-butyl, tert-butyl, n-pentyl radical, An isopentyl radical, a neopentyl radical, 1, 2-dimethyl propyl group, n-hexyl group, 1, 3-dimethyl butyl, 1-isopropyl propyl group, 1, 2-dimethyl butyl, The alkyl group of straight chains, such as n-heptyl radical, 1, 4-dimethyl pentyl radical, a 2-methyl-1-isopropyl propyl group, a 1-ethyl-3-methylbutyl radical, n-octyl radical, and a 2-ethylhexyl radical, or the letter of branching; annular alkyl groups, such as a cyclohexyl radical, etc. are mentioned. As an aralkyl radical of carbon numbers 7-20, benzyl, a phenethyl radical, etc. are mentioned, for example. As a halogen atom, for example, a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, etc. are mentioned, and it is desirable that it is a fluorine atom.

[0016] the above R1 and R2 And R3 the phenyl group which can be set, the alkyl group of carbon numbers 1-20, or the aralkyl radical of carbon numbers 7-20 -- a substituent -- one piece -- or you may have two or more pieces. As such a substituent, a halogen atom, an acyl group, an alkyl group, an alkoxy group, a halogenation alkoxy group, a nitro group, the amino group, an alkylamino radical, an alkyl carbonylamino radical, an arylamino radical, an aryl carbonylamino radical, a carbonyl group, an alkoxy carbonyl group, etc. are mentioned, for example.

[0017] In M in the above-mentioned general formula (2), a non-metal means that they are atoms other than a metal, for example, two hydrogen atoms. It becomes the structure which the hydrogen atom has specifically combined with two nitrogen atoms which exist in the central part of phthalocyanine structure, which may have a substituent, and which face. As a metal, iron, magnesium, nickel, cobalt, copper, palladium, zinc, vanadium, titanium, an indium, tin, etc. are mentioned, for example. As a metallic oxide, titanyl, vanadyl, etc. are mentioned, for example. As a metal halogenide, an aluminum chloride, indium chloride, a germanium chloride, chlorination tin, a silicon chloride, etc. are mentioned, for example. As M, it is desirable that they are a metal, a metallic oxide, or a metal halogenide, and, specifically, nickel, cobalt, copper, zinc, iron, vanadyl, dichloro tin, etc. are mentioned. They are zinc,

cobalt, vanadyl, and dichloro tin more preferably.

[0018] as a desirable gestalt of a compound expressed with the above-mentioned general formula (2), 4-8 of eight beta are the same -- or -- differing -- SR1 Or OR2 It is expressing. all of eight beta are the same more preferably -- or -- differing -- SR1 Or OR2 It is expressing. As such near infrared ray absorptivity coloring matter, for example ZnPc(PhS)8 3 (PhNH) F5, ZnPc(PhS)8 4 (PhNH) F4 and ZnPc(PhS)8 5 (PhNH) F3, ZnPc(PhS)8 4 (PhCH2 NH) F4 and ZnPc(PhS)8 5 (PhCH2 NH) F3, ZnPc(PhS)8 6 (PhCH2 NH) F2, CuPc(PhS)8 7 (PhNH) F, CuPc(PhS)8 6 (PhNH) F2, CuPc(PhS)8 5 (PhNH) F3, and VOPc(PhO)8(PhCH2 NH)5 F3, VOPc(PhO)8 6 (PhCH2 NH) F2 and VOPc(PhO)8 8 (PhCH2 NH), VOPc(PhS)8 8 (PhCH2 NH) and VOPc8 (2, 5-Cl2 PhO) (CH3) 4 {Ph(CH3) CHNH}3 F, VOPc(2, 5-Cl2 PhO)8 {Ph (CH3) 4 (CH2 NH)4 --} CuPc(2, 5-Cl2 PhO)8 {2 and 6-(CH3)2 PhO}4 {Ph (CH2 NH)4 --} CuPc8 (PhS) {2 and 6-(CH3)2 PhO}4 4 (PhCH2 NH), VOPc (CH3)8 (4-CNPhO) (CH3) 4 4, ZnPc (the phthalocyanine compound expressed with the abbreviated name of 2 and 6-Cl2 PhO}8 {2, 6-Br2-4-(CH3) PhO} 4 {Ph(CH3) CHNH}3 F is mentioned.) moreover, four of eight alpha are the same also in these compounds -- or -- differing -- OR2 Or with the compound showing a halogen atom For example, ZnPc(PhS)83(PhNH)F5 and ZnPc(PhS)8 4 (PhNH) F4, ZnPc(PhS)8 4 (PhCH2 NH) F4 and VOPc8 (2, 5-Cl2 PhO) (CH3) 4 {Ph(CH3) CHNH}3 F, VOPc(2, 5-Cl2 PhO)8 {Ph (CH3) 4 (CH2 NH)4 --} CuPc(2 5-Cl2PhO)8 {Ph (CH3) 4 (CH2NH)4 --} CuPc8 (PhS) {2 and 6-(CH3)2 PhO}4 4 (PhCH2 NH), VOPc (CH3)8 (4-CNPhO) (CH3) 4 4, ZnPc (2, the compound generally expressed with the abbreviated name of 6-Cl2 PhO}8 {2, 6-Br2-4-(CH3) PhO}4 {Ph(CH3) CHNH}3F are mentioned.)

[0019] It is desirable to consider as 0.0005 - 20 weight section, for example to the binder resin 100 weight section as amount of the above-mentioned near infrared ray absorptivity coloring matter used. When there is a possibility that near infrared ray absorptivity ability with the sufficient near infrared ray absorptivity paint film formed from a near infrared ray absorptivity resin constituent as it is under the 0.0005 weight section may not be demonstrated and 20 weight sections are exceeded, there is a possibility that the physical properties of a near infrared ray absorptivity paint film may fall. More preferably, it is 0.0015 - 10 weight section, and is 0.002 - 7 weight section still more preferably. Moreover, it is desirable to set up suitably with the thickness of a near infrared ray absorptivity paint film, for example, it is desirable to consider as 0.5 - 20 weight section by 10 micrometers in thickness, and it is more desirable to consider as 1.0 - 10 weight section. When considering as a near infrared ray absorptivity paint film with a thickness of 3mm, it is desirable to consider as the 0.002 - 0.06 weight section, and it is more desirable to consider as the 0.005 - 0.03 weight section. It is desirable to consider as the 0.0005 - 0.02 weight section by 10mm in thickness, and it is more desirable to consider as the 0.0010 - 0.01 weight section. Furthermore, as weight contained in per unit area of a near infrared ray absorptivity paint film, it is 0.01 - 2.4 g/m2, for example. Carrying out is desirable. There is a possibility that an operation of near infrared ray absorptivity coloring matter may not fully be demonstrated as they are less than two 0.01 g/m, and it is 2.4 g/m2. When it exceeds, there is a possibility that the manufacturing cost of a near infrared ray absorptivity paint film may become high. more -- desirable -- 0.05 - 1.0 g/m2 it is .

[0020] It is desirable that the water absorption of a paint film is below 2 mass % in this invention. Moreover, it is so desirable that the water absorption of a paint film is close to 0 mass %. When the water absorption of a paint film exceeds 2 mass %, the content of the water in a near infrared ray absorptivity paint film cannot be decreased, and there is a possibility that the operation effectiveness of this invention cannot be demonstrated so that degradation of near infrared ray absorptivity coloring matter can fully be controlled. More preferably, it is below 1 mass % and is below 0.8 mass % still more preferably. The water absorption of a paint film shows the weight rate (mass %) which increases when the paint film (coating film) formed with the near infrared ray absorptivity resin constituent which blended a curing agent, various additives, etc. according to the near infrared ray absorptivity coloring matter and the need other than binder resin contains water with the passage of time. The water absorption of a paint film is computed using the following type by the following measuring method.

[0021] Weight (W0) is measured for coating **** 3cmx3cm with a measuring method thickness [of the water absorption of a paint film] of 1mm after 12-hour desiccation at 80 degrees C under the reduced

pressure condition of 30 or less mPas, and let this be initial value. Subsequently, after being immersed in water and saving for 20 days at a room temperature (25 degrees C), it takes out and weight (W1) is measured. The water absorption of a paint film is computed using the following type.

Water absorption (mass %) = $\{(W1 - W0) / W0\} \times 100$ [0022] of a paint film In addition, it is possible to measure the water absorption of a paint film on certain conditions by drying the prepared near infrared ray absorptivity resin constituent for measurement of the water absorption of a paint film on the conditions shown to the base material of glass after coating that desiccation thickness is set to 1mm at the following, for example, and using for it the paint film exfoliated and produced from the base material in this invention. Moreover, although there are two kinds of operation gestalten, the case where make resin and a curing agent construct a bridge and it considers as a hardening paint film about a curing agent, and when considering without a curing agent as a dry paint film, in this invention In making a curing agent construct a bridge and considering as a hardening paint film, a curing agent as shown below is blended, a near infrared ray absorptivity resin constituent is prepared, and it becomes possible by producing a paint film on condition that the following, and presenting measurement of water absorption to measure the water absorption of a paint film under certain conditions. The paint film (coating film) production conditions for water absorption measurement are shown concretely below.

(1) With no curing agent (lacquer)

desiccation condition: -- 80 degrees C -- after 3 minutes and 50 degrees C -- the class:Sumitomo Bayer urethane company make of a seven-day curing-agent [(2)]:isocyanate compound curing agent, and "Sumi Joule N3200" (trade name)

curing agent loadings: -- hydroxyl-group =1/1 (mole ratio) hardening condition: of the isocyanate radical / binder resin of a curing agent -- 80 degrees C -- after 3 minutes and 50 degrees C -- the product made from class:Mitsui SAITEKKU of a seven-day curing-agent [(3)]:aminoplast resin curing agent, and "Cymel 325" (trade name)

Curing catalyst: Product made from Mitsui SAITEKKU, "catalyst 296-9" (trade name)

Curing-agent loadings: Binder resin / curing agent / curing catalyst =80/19/1 (solid content weight ratio)

Hardening conditions: It is 110 degrees C and is 30 minutes [0023]. It is desirable that the glass transition temperature (Tg) of the above-mentioned binder resin is -80-160 degrees C in this invention again. By this, the weatherability of binder resin itself will improve, and while the near infrared ray absorptivity ability of a near infrared ray absorptivity paint film continues conjointly with controlling the content of the water in a near infrared ray absorptivity paint film, the weatherability and the physical properties of the near infrared ray absorptivity paint film itself will improve more. Preferably, it is -50-130 degrees C, and it is 20-110 degrees C, and is 40-100 degrees C still more preferably.

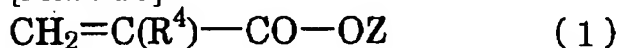
[0024] As a class of the above-mentioned binder resin, for example Acrylic (meta) resin, Acrylic urethane system resin, polyvinyl chloride system resin, polyvinylidene chloride resin, (Meta) Melamine system resin, urethane system resin, styrene resin, alkyd system resin, Phenol system resin, epoxy system resin, polyester system resin, and acrylic (meta) silicone system resin, Alkyl polysiloxane system resin, silicone resin, silicone alkyd resin, Denaturation silicone resin, such as silicone urethane resin, silicone polyester resin, and silicone acrylic resin, Fluororesin, such as polyvinylidene fluoride and a fluoro olefin vinyl ether polymer, etc. may be mentioned, thermoplastics is sufficient, and hardenability resin, such as thermosetting resin, moisture hardenability resin, ultraviolet-rays hardenability resin, and electron ray hardenability resin, is sufficient. Moreover, organic system binder resin, such as synthetic rubber, such as ethylene-propylene copolymerization rubber, polybutadiene rubber, a styrene butadiene rubber, and acrylonitrile-butadiene rubber, or natural rubber; binder resin with inorganic conventionally well-known system binders, such as a silica sol, alkali silicate, a silicon alkoxide, and those (hydrolysis) condensates, phosphate, etc. is mentioned. These may be used independently and may use two or more sorts together. It is desirable that it is fluororesin, such as denaturation silicone resin, such as acrylic (meta) resin, acrylic (meta) urethane system resin, acrylic (meta) silicone system resin, silicone resin, silicone alkyd resin, silicone urethane resin, silicone polyester resin, and silicone acrylic resin, polyvinylidene fluoride, and a fluoro olefin vinyl ether polymer, at the point of being able to dry at low temperature comparatively, being able to form a near infrared ray absorptivity paint film, and moreover

excelling in the weatherability of binder resin itself also in these. It is acrylic (meta) resin more preferably. In addition, acrylic resin and methacrylic system resin are also called acrylic resin.

[0025] At this invention, the above-mentioned binder resin is the following general formula also in the above-mentioned (meta) acrylic resin (1).;

[0026]

[Formula 5]



[0027] (R⁴ expresses a hydrogen atom or a methyl group among a formula.) Z expresses the hydrocarbon group of carbon numbers 4-25. It is desirable when the polymer which comes to carry out the polymerization of the monomer component which makes indispensable the monomer expressed is used as binder resin. One sort of monomers expressed with a general formula (1) may be used, and may use two or more sorts together. Since it becomes what was excellent also in the weatherability of binder resin itself by this in addition to the endurance of near infrared ray absorptivity coloring matter improving, the weatherability of a near infrared ray absorptivity paint film can be raised more. In this case, the above-mentioned near infrared ray absorptivity paint film will be formed from the near infrared ray absorptivity resin constituent containing the polymer which comes to carry out the polymerization of the monomer component containing the monomer expressed with the above-mentioned general formula (1), and will become.

[0028] As a hydrocarbon group of the carbon numbers 4-25 expressed with Z, polynuclear hydrocarbon radicals, such as an alkyl group; bornyl radical of straight chains, such as alicyclic hydrocarbon radical; butyls, such as a cyclohexyl radical, a methylcyclohexyl radical, and cyclo dodecyl, an isobutyl radical, tert-butyl, a 2-ethylhexyl radical, a heptyl radical, an octyl radical, a nonyl radical, a decyl group, an undecyl radical, dodecyl, a pentadecyl group, and an octadecyl radical, or a branched chain and an isobornyl radical etc. be mentioned among the above-mentioned general formula (1), for example Also in these, it is desirable that they are an alicyclic hydrocarbon radical, the alkyl group of a branched chain, and a with a carbon numbers of six or more straight chain alkyl group. Furthermore, it is a with a carbon numbers of six or more alicyclic hydrocarbon radical preferably.

[0029] As a monomer expressed with the above-mentioned general formula (1), cyclohexyl (meta) acrylate, methylcyclohexyl (meta) acrylate, cyclo dodecyl (meta) acrylate, tert-butyl cyclohexyl (meta) acrylate, isobutyl (meta) acrylate, tert-butyl (meta) acrylate, lauryl (meta) acrylate, isobornyl (meta) acrylate, stearyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, etc. are mentioned, for example.

[0030] It is desirable to carry out to more than 30 mass %, for example as amount of the monomer used expressed with the above-mentioned general formula (1), if all monomer components are made into 100 mass %. There is a possibility that the weatherability of binder resin itself may not fully improve that it is under 30 mass %. It is more than 40 mass %, and still more preferably, it is more than 60 mass %, and is more than 80 mass % most preferably. It is not limited especially as other copolymerizable partial saturation monomers which can be used for the above-mentioned monomer component, for example, the following monomer etc. is mentioned. These may be used independently and may use two or more sorts together.

[0031] Alkyl-acid-phosphate system partial saturation monomer; 2-hydroxyethyl (meta) acrylate, such as partial saturation monomer; 2-(meta) AKURIRO yloxy ethyl acid phosphate which has carboxyl groups, such as an acrylic acid, an itaconic acid, and a maleic anhydride, (Meta) Hydroxypropyl (meta) acrylate, hydroxy butyl (meta) acrylate, caprolactone denaturation hydroxy (meta) acrylate (for example, the Daicel Chemical Industries, Ltd. make --) The partial saturation monomer which has a radical with active hydrogen, such as a trade name "the plaque cel FM"; Methyl (meta) acrylate, Acrylic ester, such as ethyl (meta) acrylate, propyl (meta) acrylate, isopropyl (meta) acrylate, and butyl (meta) acrylate (meta); the partial saturation monomer which has epoxy groups, such as glycidyl (meta) acrylate.

[0032] Acrylamide, N, and N'-dimethylaminoethyl (meta) acrylate, (Meta) The partial saturation monomer which has nitrogen atoms, such as N and N-diethylaminoethyl (meta) acrylate and imide

(meta) acrylate; Ethylene glycol di(metha)acrylate, Triethylene glycol di(metha)acrylate, Tori propyleneglycol di(meth) acrylate, The partial saturation monomer which has halogen atoms, such as a partial saturation monomer; vinyl chloride which has two or more polymerization nature double bonds, TORIMECHI roll pro pantry (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, etc.; Styrene, aromatic series partial saturation monomers [, such as alpha methyl styrene,]; -- vinyl ester [, such as vinyl acetate,]; -- vinyl ether.

[0033] This invention is also the near infrared ray absorptivity resin constituent which comes to contain the polymer which comes to carry out the polymerization of the monomer component which contains the monomer expressed with the near infrared ray absorptivity coloring matter which has absorption maximum wavelength in 780nm - 1200nm, and the above-mentioned general formula (1) again more than 30 mass %. Such a near infrared ray absorptivity resin constituent will be suitably used as a resin constituent which forms the near infrared ray absorptivity paint film of this invention.

[0034] In this invention, a polymerization nature ultraviolet absorption nature monomer and a polymerization nature ultraviolet-rays stability monomer can be used as a partial saturation monomer which carries out copolymerization to binder resin for the weatherproof improvement in a near infrared ray absorptivity paint film. What is necessary is just to use the partial saturation monomer which has ultraviolet absorption nature machines, such as a benzotriazol system, a benzophenone system, and a triazine system, for the near infrared ray absorptivity paint film of this invention, especially when ultraviolet-rays cutoff ability is still more nearly required. "RUVA93" (a trade name, the Otsuka chemistry company make), "BP-1A" (a trade name, the Osaka organic chemistry company make), etc. are specifically mentioned, and these can be used independently and also they may be used as occasion demands, combining two or more sorts suitably. Moreover, what is necessary is just to use the partial saturation monomer which has the ultraviolet-rays stability radical which has a steric hindrance piperidine radical, when the further weatherproof improvement in binder resin is required. "ADEKA stub LA-82", "ADEKA stub LA-87" (all are a trade name and the Asahi Denka Kogyo K.K. make), etc. are specifically mentioned, and these can be used independently and also they may be used as occasion demands, combining two or more sorts suitably.

[0035] For example, it can carry out with a polymerization method with conventionally well-known solution polymerization, a distributed polymerization, a suspension polymerization, an emulsion polymerization, etc., using a polymerization initiator as a polymerization method for manufacturing the above-mentioned binder resin. an organic solvent which it was not limited especially as a solvent in the case of performing solution polymerization, for example, was mentioned above -- one sort -- or two or more sorts can be used. What is necessary is just to set up suitably with polymerization conditions, the weight rate of the polymer in binder resin, etc. as amount of the solvent used.

[0036] It is not limited especially as the above-mentioned polymerization initiator, for example, the usual radical polymerization initiators, such as 2 and 2'-azobis - (2-methyl butyronitrile), tert-butyl peroxy-2-ethylhexanoate, 2,2'-azobis isobutyronitrile, benzoyl peroxide, and G tert-butyl peroxide, are mentioned. These may be used independently and may use two or more sorts together. Although what is necessary is just to set up suitably as the amount used from the characteristic value of the polymer for which it asks etc., it is desirable to consider as 0.01 to 50 mass % for example, if a monomer component is made into 100 mass %. It is 0.05 to 20 mass % more preferably.

[0037] As polymerization conditions in the above-mentioned polymerization method, it is not limited especially that what is necessary is just to set up suitably with a polymerization method. For example, as polymerization temperature, it is desirable to consider as room temperature -200 degree C. It is 40-140 degrees C more preferably. What is necessary is just to set up suitably as reaction time, according to the presentation of a monomer component, the class of polymerization initiator, etc., so that a polymerization reaction may be completed.

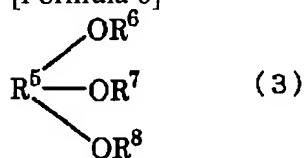
[0038] As number average molecular weight of the polymer which constitutes the above-mentioned binder resin, it is desirable that it is 1000-100000 for example. More preferably, it is 2000-80000 and is 4000-60000 still more preferably. In addition, weight average molecular weight is the measured value standard [GPC] for polystyrene.

[0039] It is desirable to consider as 50 to 99.9995 mass % as amount of the above-mentioned binder resin used, for example, if near infrared ray absorptivity resin constituent 100 mass %. If there is a possibility that the physical properties of the near infrared ray absorptivity paint film formed from a near infrared ray absorptivity resin constituent as it is under 50 mass % may become less enough and 99.9995 mass % is exceeded, since the weight rate of near infrared ray absorptivity coloring matter will decrease, there is a possibility that the near infrared ray absorptivity ability of a near infrared ray absorptivity paint film may become less enough. More preferably, it is 60 to 99.9985 mass %, and is 70 to 99.998 mass % still more preferably.

[0040] As for the near infrared ray absorptivity paint film of this invention, it is still more desirable to come to contain a dehydrating agent. Thereby, the content of the water in a near infrared ray absorptivity paint film can be effectively controlled with binder resin. Although there are various things in an inorganic compound or an organic compound as a dehydrating agent, when using for this invention, the direction which volatilizes at the time of paint film formation, and does not remain after formation is desirable at a point without the degradation of a paint film. It is good to use the dehydrating agent of an organic system which is comparatively easy to volatilize at such a point. As an example of such a dehydrating agent, hydrolysis nature ester compounds, such as ORUTOGI acid TORIMECHIRU, a triethyl orthoformate, alt.acetic-acid TORIMECHIRU, alt.acetic-acid triethyl, methyl trimetoxysilane, gamma-methacryloxypropyl trimethoxy silane, vinyltrimetoxysilane, methyl silicate, and ethyl silicate, are mentioned, and one sort or two sorts or more can be used. The desirable gestalt of the chemical structure of such a dehydrating agent is for example, the following general formula (3).;

[0041]

[Formula 6]



[0042] (-- the inside of a formula, R5, R6, R7, and R8 are the same -- or it differs, the organic radical of carbon numbers 1-8 is expressed, and it is the organic radical of carbon numbers 1-3 preferably.) -- it is expressed. Moreover, it is desirable to consider as 1 - 20 weight section, for example to the binder resin 100 weight section as amount of the dehydrating agent used. When there is a possibility that the operation effectiveness of a dehydrating agent cannot fully be demonstrated as it is under 1 weight section and 20 weight sections are exceeded, there is a possibility that the physical properties of a near infrared ray absorptivity paint film may fall. More preferably, it is 2 - 10 weight section, and is 3 - 7 weight section still more preferably.

[0043] Although it is usable that are not constructed [bridge formation or / either] a bridge as for the near infrared ray absorptivity paint film of this invention, it is more desirable for it to have been desirable, for example, for itself to have constructed the bridge independently, or for the bridge formation paint film to have blended the cross linking agent, and to form a hardening paint film in respect of the improvement in endurance of coloring matter. According to the class of the application for which it is used, or cross linking agent, the near infrared ray absorptivity resin constituent which will form the near infrared ray absorptivity paint film of this invention can be stiffened on various hardening conditions, and can be used as a room-temperature-setting mold, a heat hardening mold, ultraviolet rays, or an electron ray hardening mold. Moreover, what is necessary is just to let especially the amount of the cross linking agent used, addition, the distributed approach, etc. be the amount used usually used for polyol, and addition and the distributed approach by the case where it is constituted by the polyol to which it is not limited, for example, binder resin has two or more hydroxyl groups in 1 intramolecular.

[0044] As the above-mentioned cross linking agent, the poly (block) isocyanate compound, aminoplast resin, etc. are mentioned by the case where binder resin is constituted by polyol, for example. These may be used independently and may use two or more sorts together.

[0045] The above-mentioned (block) poly isocyanate compound means the poly isocyanate compound and/or a block poly isocyanate compound. It will not be limited especially if it is the compound which has at least two isocyanate radicals in intramolecular as the above-mentioned poly isocyanate compound. For example, tolylene diisocyanate, xylylene diisocyanate, Diphenylmethane diisocyanate, 1,6-hexamethylene diisocyanate, Isophorone diisocyanate, 4,4'-methylenebis (cyclohexyl isocyanate), Lysine diisocyanate, trimethyl hexamethylene di-isocyanate, 1, 3-(isocyanate methyl) cyclohexane, 1,5-naphthalene diisocyanate, Poly isocyanates, such as triphenylmethane triisocyanate; the derivative (denaturation object) of the poly isocyanates, such as an adduct object of such poly isocyanates, a buret object, and an isocyanurate object, etc. is mentioned.

[0046] In order to make a bridge construct when carrying out stoving of the near infrared ray absorptivity resin constituent to the above-mentioned block poly isocyanate compound, and to raise the storage stability in ordinary temperature, the isocyanate radical of the poly isocyanate compound is usually blocked by the blocking agent. It is not limited especially as the above-mentioned blocking agent, for example, compounds, such as epsilon caprolactam, a phenol, cresol, an oxime, and alcohol, etc. are mentioned. As a commercial item of the above-mentioned (block) poly isocyanate compound, Sumi Joule N3200, Sumi Joule N3300, Sumi Joule BL3175, Desmodur N3400, Desmodur N3600, Desmodur VPLS2102 (a trade name, the Sumitomo Bayer urethane company make), duranate E-402-90T (a trade name, Asahi Chemical Industry Co., Ltd. make), etc. are mentioned, for example. Moreover, in order to prevent yellowing of the near infrared ray absorptivity paint film formed from a near infrared ray absorptivity resin constituent, the non-xanthochroism poly isocyanate compound which does not have the isocyanate radical coupled directly with the ring is desirable.

[0047] Although not limited especially as amount of the above-mentioned (block) poly isocyanate compound used, it is desirable to make it the isocyanate radical in the poly (block) isocyanate compound become 0.6-1.4 mols to one mol of hydroxyl groups in binder resin for example. If it is less than 0.6 mols, since many hydroxyl groups of a reaction remain at last in a near infrared ray absorptivity resin constituent, the weatherability of the near infrared ray absorptivity paint film formed using the near infrared ray absorptivity resin constituent obtained may fall. When it exceeds 1.4 mols, many unreacted isocyanate radicals in a near infrared ray absorptivity paint film may remain, and a paint film may cause [this] foaming and milkiness in response to the time of paint film hardening with the moisture in air. It is 0.8-1.2 mols more preferably.

[0048] The above-mentioned aminoplast resin is the addition condensation object of the compound and formaldehyde which have amino groups, such as a melamine and guanamine, and is also called amino resin. It is not limited especially as the above-mentioned aminoplast resin. For example, a dimethylol melamine, Trimethylolmelamine, a tetra-methylol melamine, a PENTA methylol melamine, A hexa methylol melamine, a perfect alkyl mold methylation melamine, a perfect alkyl mold butyl-ized melamine, A perfect alkyl mold isobutyl-ized melamine, a perfect alkyl mold mixed ether-ized melamine, A methylol type methylation melamine, an imino group mold methylation melamine, a methylol type mixed ether-ized melamine, Melamine resin, such as an imino group mold mixed ether-ized melamine; guanamine resin, such as butyl-ized benzoguanamine, methyl / ethyl mixing alkylation benzoguanamine, methyl / butyl mixing alkylation benzoguanamine, and butyl-ized glycoluril, etc. is mentioned.

[0049] As a commercial item of the above-mentioned aminoplast resin, Cymel 1128, Cymel 303, the my coat 506, Cymel 232, Cymel 235, Cymel 771, Cymel 325, Cymel 272, Cymel 254, Cymel 1170 (all are a trade name and a product made from Mitsui SAITEKKU), etc. are mentioned, for example.

[0050] It is desirable to blend so that it may not be limited especially as amount of the above-mentioned aminoplast resin used, for example, the solid content weight ratio of binder resin and aminoplast resin may be set to 9 / 1 - 6/4. When binder resin becomes less than 6/4, the near infrared ray absorptivity paint film obtained becomes hard too much, and there is a possibility that the engine performance of a paint film may fall. If binder resin increases in number more than 9/1, since bridge formation will not fully progress, there is a possibility that the near infrared ray absorptivity paint film obtained may become a thing inferior to a water resisting property or solvent resistance.

[0051] a curing catalyst for the above-mentioned near infrared ray absorptivity resin constituent to promote the crosslinking reaction of binder resin and a cross linking agent if needed -- one sort -- or two or more sorts may also be included. Although not limited especially as such a curing catalyst, it is desirable to, use catalysts, such as a dibutyl tin JIRAU rate and tertiary amine, for example, in using the above-mentioned (block) poly isocyanate compound, and when using the above-mentioned aminoplast resin, it is desirable to use an acid or basic curing catalyst.

[0052] as the compound except having mentioned above in the near infrared ray absorptivity resin constituent which will form the near infrared ray absorptivity paint film of this invention -- for example, a solvent, an additive, etc. -- one sort -- or two or more sorts may be included. The organic solvent same with having mentioned above as such a solvent etc. is mentioned. As an additive The well-known additive generally used for the resin constituent which forms a film, the coating film, etc. can be used conventionally. For example, a leveling agent; Non-subtlety particles, such as a colloid silica and alumina sol, A defoaming agent, a dripping nature inhibitor, a silane coupling agent, a titanium white, a multiple oxide pigment, pigment; pigment agent;, such as carbon black, an organic pigment, and pigment intermediate field, -- an anti-oxidant; viscosity modifier; UV stabilizer; metal-deactivator; peroxide decomposition agent --; bulking agent; reinforcing agent; plasticizer; lubricant; anticorrosives; rust-proofer; fluorescence brightening agent; organic and an inorganic system ultraviolet ray absorbent - inorganic system heat ray absorbent; -- organic and inorganic flame proofing agent; -- an antistatic agent etc. is mentioned.

[0053] As a use gestalt of the near infrared ray absorptivity paint film of this invention, the layered product prepared on the transparence base material, the layered product inserted with the transparence base material of two sheets are mentioned by using as a near infrared ray absorption layer the near infrared ray absorptivity paint film formed from a near infrared ray absorptivity resin constituent, for example. It is not limited especially as the above-mentioned transparence base material, for example, inorganic system base materials [, such as organic system base material; glass,], such as polycarbonate resin, acrylic resin, polyethylene resin, polyester system resin, polypropylene resin, polystyrene resin, and polyvinyl chloride resin, are mentioned. Moreover, the above and a transparence base material may be colored and various designs may be printed.

[0054] As the formation approach of the above-mentioned near infrared ray absorption layer, (1) near-infrared-ray absorptivity resin constituent is applied on a transparence substrate, for example. The approach and (2) near-infrared-ray absorptivity resin constituent which are made to harden the near infrared ray absorptivity resin constituent applied after that, and form a near infrared ray absorption layer are fabricated and film-ized, the approach of making it into a layered product by sticking on a transparence base material etc. is mentioned, and it is desirable from the approach of (1) being simple.

[0055] In the formation approach of the above-mentioned near infrared ray absorption layer, approaches, such as immersion, blasting, brush coating, a curtain flow coat, a gravure coat, a roll coat, a spin coat, a blade coat, a bar coat, a reverse coat, a die coat, a spray coat, and electrostatic coating, are mentioned, for example as an approach of applying a near infrared ray absorptivity resin constituent on a transparence base material. It can be made to be able to mix suitably and the organic solvent mentioned above to the near infrared ray absorptivity resin constituent in these cases can be applied. Moreover, as an approach of stiffening a near infrared ray absorptivity resin constituent, the approach of heating, the approach of irradiating ultraviolet rays and an electron ray, etc. are mentioned that what is necessary is just to set up suitably according to the class of binder resin etc.

[0056] As thickness of the above-mentioned near infrared ray absorption layer, it is not limited that what is necessary is just to especially set up suitably by a use application etc. For example, it is desirable to make the thickness at the time of desiccation set to 0.5-1000 micrometers. It is 1-100 micrometers more preferably. Furthermore, 1-50 micrometers is 1-20 micrometers especially preferably.

[0057] In the above-mentioned layered product, it is desirable to prepare an ultraviolet absorption layer in the optical incidence side of a near infrared ray absorption layer. Thereby, degradation of the near infrared ray absorptivity coloring matter by sunlight can be controlled more effectively. The gestalt by which the laminating was carried out to the order of an ultraviolet absorption layer, a base material, and

a near infrared ray absorption layer is mentioned from gestalt [by which was not limited especially as a laminated structure of such a layered product, for example, the laminating was carried out to the order of an ultraviolet absorption layer, a near infrared ray absorption layer, and a base material from (1) light incidence side], and (2) light incidence side. Moreover, in order to raise abrasion-proof nature and resistance to contamination, surface protective layers, such as a rebound ace court layer of a silicon system or an organic system and photocatalyst stratum functionale, may be further prepared in a layered product front face, and a primer layer may be prepared between a base material and a layered product and between each class of a layered product as occasion demands. It is not limited especially as a presentation or thickness of such an ultraviolet absorption layer, or a surface protective layer and a primer layer.

[0058] The near infrared ray absorptivity paint film of this invention is characterized by there being little degradation of near infrared ray absorptivity ability again, as physical properties which a paint film has, there are few falls of the near infrared ray absorptivity ability of the near infrared ray absorptivity coloring matter after an accelerated weathering test, namely, it is mentioned that an absorbing-power survival rate is high, and the near infrared ray absorbing-power survival rate of 63 degrees C of optical exposures in the accelerated weathering test in ultraviolet-rays auto fade meter and 48 hours after is 50% or more. The absorbing-power survival rate which specifically performs the accelerated weathering test in ultraviolet-rays fade meter using the paint film formed using the near infrared ray absorptivity resin constituent, and is searched for by the following evaluation approach is 50% or more. It is 60% or more and is 80% or more still more preferably 70% or more more preferably. In addition, actual measurement of a near infrared ray absorptivity ability survival rate will be performed by the paint film with which the base material which does not have absorption in near infrared ray fields, such as glass and a PET film, was coated.

[0059] On the evaluation approach base material of a near infrared ray absorbing-power survival rate, a near infrared ray absorptivity paint film is formed, and the permeability of the light in the absorption maximum wavelength in the near infrared region of the obtained layered product is measured with a spectrophotometer (Ti initial value). Moreover, the permeability in the wavelength concerned of a base material is measured (T0). Using this layered product, continuous irradiation is performed at 63 degrees C for 48 hours, the irradiation test in ultraviolet-rays auto fade meter (the Suga Test Instruments Co., Ltd. make, trade name "FAL-AU-B") is made into an accelerated weathering test, and the permeability in the absorption maximum wavelength in the near infrared region after a trial is measured (T). From such measured value, absorbing-power survival rate R (%) is calculated by the degree type.

$$R(\%) = (T_0 - T) / (T_0 - T_i)$$

[0060] As for the layered product which contains the near infrared ray absorptivity paint film of this invention, and this near infrared ray absorptivity paint film as a near infrared ray absorptivity layer, it is desirable to make transparency high, for example, it is desirable to make a haze (haze value) into 3.0% or less. More preferably, it is 2.0% or less and is 1.0% or less still more preferably. Such a near infrared ray absorptivity paint film and a layered product can be used suitable for the object for the apertures of cars, such as an object for the apertures of a building or a residence, an electric car, and an automobile, an arcade, a greenhouse, etc., and also they can be used for the object for infrared remote control incorrect actuation prevention in a plasma display, the object for protection of a solar panel, sunglasses, common glasses, safety goggles, a contact lens, etc. Moreover, it can also be used, being able to apply a near infrared ray absorptivity resin constituent to the above-mentioned goods or the part of a request of the structure (to for example, glass sides, such as an aperture).

[0061]

[Example] Although an example is given to below and this invention is further explained to a detail, this invention is not limited only to these examples.

[0062] Toluene 84g was added to the 500ml flask equipped with synthetic example 1 agitator, dropping opening, the thermometer, the cooling pipe, and the nitrogen gas inlet, and it heated at 105 degrees C. It is 2 and 2'-azobis to this as 69g [of cyclohexyl methacrylate], 16.5g [of 2-ethylhexyl acrylate], 0.5g [of methacrylic acids], and methacrylic-acid 2-hydroxyethyl 14g, and an initiator. - (2-methyl

butyronitrile) Continuation dropping was carried out over 3 hours, and 2g was heated for further 2 hours. Then, toluene 18g was added and 50% solution of acrylic resin was obtained. In addition, the number average molecular weight of the polymer which constitutes this acrylic resin was 5800. The presentation of the monomer component used for composition of acrylic resin and the acquired characteristic value of acrylic resin are shown in Table 1.

[0063] Acrylic resin was obtained by the same approach as the synthetic example 1 except the presentation of the monomer component used for composition of the synthetic examples 2 and 4 and 5 acrylic resin having been shown in Table 1. The characteristic value of the obtained acrylic resin is shown in Table 1.

[0064] Toluene 84g was added to the 500ml flask equipped with synthetic example 3 agitator, dropping opening, the thermometer, the cooling pipe, and the nitrogen gas inlet, and it heated at 115 degrees C. To this, as 81g of cyclohexyl methacrylate, 18.5g of 2-ethylhexyl acrylate, 0.5g of methacrylic acids, and an initiator, carried out continuation dropping, having applied 1g of t-butylperoxy-2-ethylhexanoate for 3 hours, it was made to heat for further 2 hours, toluene 18g was added after that, and 50% solution of acrylic resin was obtained. In addition, the number average molecular weight of the polymer which constitutes this acrylic resin was 17000. The presentation of the monomer component used for composition of acrylic resin and the acquired characteristic value of acrylic resin are shown in Table 1.

[0065] Acrylic resin was obtained by the same approach as the synthetic example 3 except the presentation of the monomer component used for composition of synthetic example 6 acrylic resin having been shown in Table 1. The characteristic value of the obtained acrylic resin is shown in Table 1.

[0066] In the 500ml flask equipped with synthetic example 7 agitator, dropping opening, the thermometer, the cooling pipe, and the nitrogen gas inlet, methyl-ethyl-ketone 100g, 2--2H-benzotriazole [2'-hydroxy-5'-(methacryloyloxy-ethyl) phenyl (a trade name "RUVA93" --)] 18g by Otsuka chemistry company g, 34g [of cyclohexyl methacrylate], and styrene 3g, 3g of 2-ethylhexyl methacrylate, 2g of butyl acrylates, and 0.2g (2 and 2'-azobis - (2-methyl butyronitrile)) of initiators were taught, and it heated to reflux temperature, introducing and stirring nitrogen gas. They are methyl ethyl ketones 80g and 2 to this. - [2'-hydroxy-5'-(methacryloyloxy-ethyl) phenyl] -2H-benzotriazole ("trade name RUVA 93" Otsuka chemistry company make) 18g, 34g [of cyclohexyl methacrylate], and styrene 3g, 3g of 2-ethylhexyl methacrylate, 2g of butyl acrylates, and the mixture of 0.2g of initiators were dropped over 2 hours, it heated for further 2 hours, and 50% solution of acrylic resin was obtained. In addition, the number average molecular weight of the polymer which constitutes this acrylic resin was 20000.

[0067] Acrylic resin was obtained by the same approach as the synthetic example 3 except the synthetic example 8 monomer component having been shown in Table 1. The characteristic value of the obtained resin is shown in Table 1.

[0068]

[Table 1]

		合成例1	合成例2	合成例3	合成例4	合成例5	合成例6	合成例8
単 体 成 分 の 組 成 (部)	1)CHMA	69	28	81	—	—	—	30
	2)2-EHA	16.5	57.5	18.5	—	—	—	9.5
	3)MMA	—	—	—	49.5	15.5	59.5	60
	4)EA	—	—	—	36	70	40	—
	5)MAA	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	6)HEMA	14	14	—	14	14	—	—
	7)開始剤1	2	2	—	2	2	—	—
	8)開始剤2	—	—	1	—	—	1	1
樹脂 溶液	不揮発分	50	49.9	50	50.1	50.2	50.1	49.8
	数平均分子量	5800	5500	17000	5700	5400	16000	16000

[0069] Table 1 is explained below.

1) CHMA is cyclohexyl methacrylate, 22-EHA is 2-ethylhexyl acrylate, 3MMA is a methyl methacrylate, 4EA is an ethyl acrylate, 5MAA is a methacrylic acid, 6HEMA is methacrylic-acid 2-hydroxyethyl, seven initiators 1 are 2 and 2'-azobis - (2-methyl butyronitrile), and eight initiators 2 are t-butylperoxy-2-ethylhexanoate.

[0070] The Sumitomo Bayer urethane company make and Sumi Joule N3200 (trade name) were mixed for the acrylic resin 10 section of the synthetic example 1, and coloring matter 1 as example 1 binder resin, the one section was mixed as the 0.23 sections, the toluene 4.3 section, and a curing agent, and the near infrared ray absorptivity resin constituent was prepared. Carried out coating of this to the PET film (the Toray Industries, Inc. make, a trade name "lumiler T60", 50 micrometers) as a base material, it was made to dry at 80 degrees C, and the near infrared ray absorption layer of 5 micrometers of thickness was formed. Moreover, as an ultraviolet absorption layer, the 0.3 sections were mixed, and coating of the acrylic resin 10 section of the synthetic example 7, the methyl-ethyl-ketone 3 section, and Sumi Joule N3200 was carried out on the above-mentioned near infrared ray absorption layer, they were dried at 80 degrees C, and the ultraviolet absorption layer of 5 micrometers of thickness was formed. The accelerated weathering test was carried out for the sample produced by the above approach after storage for seven days at 50 degrees C. Moreover, the haze (haze value) of a test sample was measured.

[0071] Production of a test sample and an accelerated weathering test were carried out by the same approach as an example 1 with the configuration of a raw material shown in examples 2-7 and nine table 2. namely, in the example 3 using the acrylic resin obtained by binder resin in the synthetic example 2 in the example 2 Sumi Joule N3200 is not blended with binder resin using the acrylic resin obtained in the synthetic example 3. In the example 4 Coloring matter 2 to near infrared ray absorption coloring matter in 0.16 ***** and the example 5 Coloring matter 3 to near infrared ray absorption coloring matter in 0.13 ***** and the example 6 The 0.5 section (OFM) of ORUTOGI acid TORIMECHIRU were added as a dehydrating agent to the acrylic resin 10 section of the synthetic example 1, except having used it one day after, the test sample was produced by the same approach as an example 1, and the accelerated weathering test was carried out. Moreover, in the example 7, except having not prepared an ultraviolet absorption layer, the test sample was produced by the same approach as an example 1, and the accelerated weathering test was carried out. In the example 9, except having not blended Sumi Joule N3200 with binder resin using the acrylic resin obtained in the synthetic example 8, and having not prepared an ultraviolet absorption layer, the test sample was produced by the same approach as an example 1, and the accelerated weathering test was carried out. Moreover, the haze (haze value) of a test sample was measured.

[0072] The near infrared ray absorption layer was formed on the PET film like example 8 example 1. Furthermore, the near infrared ray absorption layer formed the ultraviolet absorption layer on the PET film of the opposite side on the same conditions as an example 1. The accelerated weathering test was carried out for this sample after storage for seven days at 50 degrees C. Moreover, the haze (haze value) of a test sample was measured.

[0073] With the configuration of a raw material shown in one to example of comparison 3 table 2, production of a trial ingredient and an accelerated weathering test were carried out by the same approach as an example 1. That is, in the example 1 of a comparison, by the example 2 of a comparison, the synthetic example 4 was used for binder resin, the synthetic example 5 was used for binder resin, except having used the synthetic example 6 for binder resin, and having not blended Sumi Joule N3200, the test sample was produced by the same approach as an example 1, and the accelerated weathering test was carried [the example 3 of a comparison] out.

[0074] The near infrared ray absorptivity resin constituent prepared in the measurement example 1 of the water absorption of the evaluation approach paint film was dried for 3 minutes at 80 degrees C after coating so that desiccation thickness might be set to 1mm, and it exfoliated from the base material, and the 3cmx3cm near infrared ray absorptivity paint film was produced. This was heated at 80 degrees C under reduced pressure conditions (about 20 mPa(s)) after preservation for seven days at 50 degrees C, and weight was measured after 12-hour desiccation (referred to as W0). It took out and weight was measured, after being immersed in water and saving this film for 20 days at a room temperature

(referred to as W1). From such measured value, water absorption was measured according to the degree type.

Water absorption of a paint film (mass %) = it measured similarly about $\{(W1-W0)/W0\} \times 100$ examples 2-8 and the examples 1-3 of a comparison. The result was shown in Table 2. Examples 3 and 9 and the example 3 of a comparison do not use a curing agent (Sumi Joule N3200).

[0075] The permeability of the light in the absorption maximum wavelength of the test sample produced by the approach of the weatherproof examples 1-9 of coloring matter and the examples 1-3 of a comparison was measured with the spectrophotometer (Ti initial value). Moreover, the permeability in the wavelength concerned of a base material film was measured (T0). Using this test sample, the continuous irradiation trial in ultraviolet-rays auto fade meter (the Suga Test Instruments Co., Ltd. make, trade name "FAL-AU-B") was performed at 63 degrees C for 48 hours, it considered as the accelerated weathering test, and the permeability in the absorption maximum wavelength after a trial was measured (T). In addition, in the irradiation test, the example 7 performed a near infrared ray absorption layer side to the optical (ultraviolet rays) exposure from the ultraviolet absorption layer side except example 7. From such measured value, near infrared ray absorbing-power survival rate R (%) was calculated by the degree type. The result was shown in Table 2.

$$R(\%) = (T0 - T) / (T0 - Ti)$$

[0076]

[Table 2]

			実施例									比較例		
			1	2	3	4	5	6	7	8	9	1	2	3
近赤外線吸収層を形成する樹脂組成物(部)	ペインダー樹脂	合成例1	10	—	—	10	10	10	10	10	—	—	—	—
		合成例2	—	10	—	—	—	—	—	—	—	—	—	—
		合成例3	—	—	10	—	—	—	—	—	—	—	—	—
		合成例4	—	—	—	—	—	—	—	—	—	10	—	—
		合成例5	—	—	—	—	—	—	—	—	—	—	10	—
		合成例6	—	—	—	—	—	—	—	—	—	—	—	10
		合成例8	—	—	—	—	—	—	—	—	10	—	—	—
	色素	色素1	0.23	0.23	0.23	—	—	0.23	0.23	0.23	0.23	0.23	0.23	0.23
		色素2	—	—	—	0.16	—	—	—	—	—	—	—	—
		色素3	—	—	—	—	0.13	—	—	—	—	—	—	—
	脱水剤	OFM	—	—	—	—	—	0.5	—	—	—	—	—	—
近赤外線吸収層の硬化剤 スミジュールN3200			1	1	—	1	1	1	1	1	—	1	1	—
紫外線吸収層を形成する樹脂組成物(部)	ペインダー樹脂	合成例7	10	10	10	10	10	10	—	10	—	10	10	10
	スミジュールN3200		0.3	0.3	0.3	0.3	0.3	0.3	—	0.3	—	0.3	0.3	0.3
評価結果	吸水率(%)		0.7	1.2	1.1	0.7	0.6	0.7	0.7	0.7	1.8	2.6	3.0	2.8
	近赤外線吸収性能残存率(%)		90	78	80	94	98	95	84	87	57	48	39	41

[0077] Table 2 is explained below. Coloring matter 1 is VOPc (2, 5-Cl₂ PhO)₈ (CH₃). 4 It is {Ph(CH₃)CHNH}₃ F. Coloring matter 2 VOPc (2, 5-Cl₂ PhO)₈ {2 and 6-(CH₃)₂ PhO}₄ 4 (PhCH₂ NH) it is -- coloring matter 3 : CuPc (2, 5-Cl₂ PhO)₈ {2 and 6-(CH₃)₂ PhO}₄ 4 (PhCH₂ NH) it is -- OFM of a dehydrating agent -- ** and ORUTOGI acid trimethyl *****.

[0078] About measurement of the haze of the test sample produced by the approach of the measurement examples 1-9 of a haze (haze value), it is JIS. According to K7105, it carried out using the hazemeter by Nippon Denshoku Co., Ltd. The result was shown in Table 3.

[0079]

[Table 3]

	実施例								
	1	2	3	4	5	6	7	8	9
ヘーズ(%)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

[0080]

[Effect of the Invention] Since the near infrared ray absorptivity paint film of this invention consists of an above-mentioned configuration, that near infrared ray absorptivity coloring matter deteriorates forms the layered product which can demonstrate the weatherability which was controlled and was excellent. Can use suitable for the object for the apertures of cars, such as an object for the apertures of a building or a residence, an electric car, and an automobile, an arcade, a greenhouse, etc., and also It can use for the object for infrared remote control incorrect actuation prevention in a plasma display, the object for protection of a solar panel, sunglasses, common glasses, safety goggles, a contact lens, etc.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

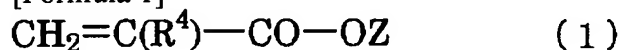
CLAIMS

[Claim(s)]

[Claim 1] The near infrared ray absorptivity paint film characterized by being a near infrared ray absorptivity paint film containing the near infrared ray absorptivity coloring matter which has absorption maximum wavelength in 780nm - 1200nm, and the near infrared ray absorbing-power survival rate 48 hours [in the accelerated weathering test in ultraviolet-rays auto fade meter] after an optical exposure being 50% or more.

[Claim 2] Said near infrared ray absorptivity paint film is the following general formula (1).;

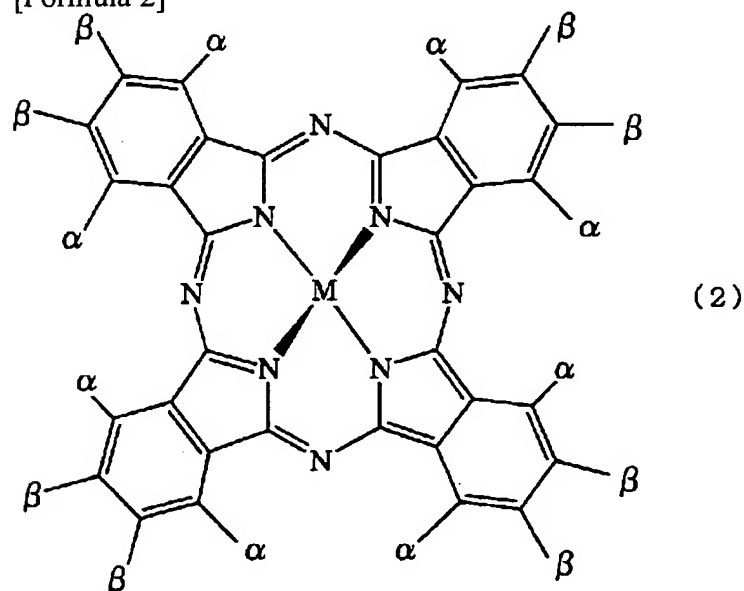
[Formula 1]



(R⁴ expresses a hydrogen atom or a methyl group among a formula.) Z expresses the hydrocarbon group of carbon numbers 4-25. Near infrared ray absorptivity paint film according to claim 1 characterized by coming to be formed from the near infrared ray absorptivity resin constituent containing the polymer which comes to carry out the polymerization of the monomer component which contains the monomer expressed more than 30 mass %.

[Claim 3] Said near infrared ray absorptivity coloring matter is the following general formula (2).;

[Formula 2]

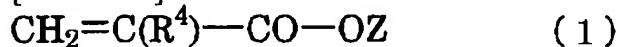


the inside of a formula and alpha are the same -- or it differs, SR1, OR2, NHR3, or a halogen atom is expressed, and NHR3 is made indispensable. R1 and R2 And R3 The aralkyl radical of the same, or the phenyl group which may differ and may have a substituent, the alkyl group of carbon numbers 1-20 or carbon numbers 7-20 is expressed. beta is the same -- or -- differing -- SR1 and OR2 or a halogen atom -

- expressing -- SR1 Or OR2 Suppose that it is indispensable. However, at least one of alpha and beta is a halogen atom or OR2. Suppose that it is indispensable. M expresses a non-metal, a metal, a metallic oxide, or a metal halogenide. Near infrared ray absorptivity paint film according to claim 1 or 2 characterized by being the compound expressed.

[Claim 4] The near infrared ray absorptivity coloring matter and the following general formula (1) which have absorption maximum wavelength in 780nm - 1200nm;

[Formula 3]



(R4 expresses a hydrogen atom or a methyl group among a formula.) Z expresses the hydrocarbon group of carbon numbers 4-25. Near infrared ray absorptivity resin constituent characterized by coming to contain the polymer which comes to carry out the polymerization of the monomer component which contains the monomer expressed more than 30 mass %.

[Translation done.]